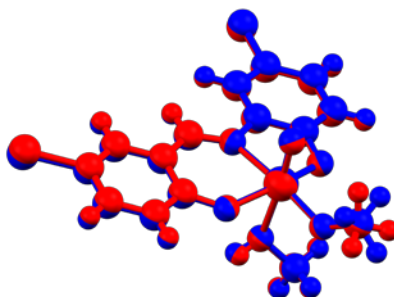


According to compare complex with similar structures two compounds selected. first complex has been published by Shahverdizadeh *et al* (CSD code GAPCUX) [1]. This compound presents the same coordination geometry and bond distances, as well as hydrogen bonding between the methanol and the oxygen of the aminophenol group (see Table S1 and Fig. S1). A second interesting compound can be compared to our compound (see Fig. 1), published by Kraehmer and Rehder (CSD code CAQJEL) [2], comparison of the three structures doesn't show differences between them.



**Fig. S1:** Overlay of the structures of [VOL(OCH<sub>3</sub>)(OHCH<sub>3</sub>)] in red at 200 K and in blue at 100 K.

**Table S1:** comparison of vanadium tridentate complexes.

CSD code:	VOL(OCH <sub>3</sub> )(OHCH <sub>3</sub> )	GAPCUX[1]	CAQJEL[2]
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<b>a</b> (Å)	10.1007(7)	9.9585(2)	7.1797(17)
<b>b</b> (Å)	9.8800(4)	9.8949(2)	21.233(5)
<b>c</b> (Å)	17.3786(11)	17.3612(3)	19.471(5)
<b>β</b> (°)	100.495(2)	100.746(2)	99.801(5)
<b>V</b> (Å <sup>3</sup> )	1705.28	1680.74	2924.96
<b>T</b> (K)	200	100	153
<b>R</b> (%)	2.8	4.63	5.71
<b>V–Ooxo</b> (Å)	1.588(2)	1.596(2)	1.587(3); 1.583(3)
<b>V–Ophenyl</b> (Å)	1.867(2)	1.872(2)	1.869(3); 1.867(3)
<b>V–Oaminophenol</b> (Å)	1.932(2)	1.937(2)	1.925(3); 1.867(3)
<b>V–Omethanol</b> (Å)	2.277(2)	2.266(2)	2.360(3); 2.359(4)
<b>V–Omethanoate</b> (Å)	1.759(2)	1.766(2)	1.764(3); 1.765(3)
<b>V–N</b> (Å)	2.173(3)	2.170(3)	2.147(4); 2.158(4)
<b>O(–H)...O</b> (Å)	2.707(2)	2.702(3)	2.804(4); 2.831(4)
<b>V–O(–H)...O</b> (°)	129.16(8)	128.7(1)	145.3(2); 144.5(2)

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- [2] V. Kraehmer, D. Rehder, *J. Chem. Soc., Dalton Trans.* 41, 5224 (2012).